

PATENT SPECIFICATION

NO DRAWINGS

870,191



Date of Application and filing Complete Specification: Nov. 4, 1958.

No. 35322/58.

Application made in United States of America on Nov. 5, 1957.

Complete Specification Published: June 14, 1961.

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International Classification:—C08f.

COMPLETE SPECIFICATION

Methyl Methacrylate-Containing Syrups and their preparations

ERRATA

SPECIFICATION No. 870,191

Page 1, line 21, for "polmerized" read
"polymerized"
Page 2, line 3, for "a" read "at"
Page 2, line 21, for "every" read "very"
Page 2, line 26, for "obtian" read "obtain"
Page 5 line 10, for "homopolymer" read
"homopolymer."

THE PATENT OFFICE

14th August, 1961

late in monomeric methyl methacrylate which has been stable, has had a useful viscosity, and has had a sufficiently high concentration of polymer such that it could be molded at a high rate to give laminated articles having good weathering, stiffness and craze-resistant properties.

According to the present invention, there is provided a polymer-in-monomer syrup wherein the said monomer is methyl methacrylate alone or with a copolymerizable α - β -ethylenically-unsaturated compound, wherein the polymer is a methyl methacrylate homopolymer or a copolymer of methyl methacrylate and a copolymerizable α - β -ethylenically-unsaturated compound, has an inherent viscosity as hereinafter defined within the range of 0.25 to 1 and is dissolved in the said monomer, and wherein the syrup has a bulk viscosity in the range 0.5 to 50 poises and contains less than

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with methyl methacrylate include vinyl acetate, styrene, alkyl acrylates, and other alkyl methacrylates. Methyl methacrylate, however, preferably constitutes at least 50% by weight of such copolymers.
The bulk viscosity of the syrup may be measured by any standard method, for instance the Gardner Tube or Brookfield Viscosimeter. The method used throughout this specification and claims has been to compare the samples with standard viscosity samples in Gardner viscosity tubes. The bulk viscosity of the syrup at 25° C. is preferably between 2 and 15 poises. The aforesaid low viscosity polymer may either be formed in sufficient monomer in situ or be prepared separately and dissolved in sufficient monomer to give the requisite bulk viscosity.

There is also provided, according to the present invention, a process comprising heating monomer in the presence of a chain transfer

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COMPLETE SPECIFICATION

Methyl Methacrylate-Containing Syrups and their preparations

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, (Assignee of WILLIAM HAROLD CALKINS, EDWARD NOONAN SQUIRE and MANDELL STANLEY ZIEGLER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methyl methacrylate-containing syrups and more particularly concerns polymer-in-monomer syrups derived from methyl methacrylate, optionally with other α - β -ethylenically-unsaturated compounds, processes for preparing such syrups, and cured products resulting therefrom.

Heretofore it has not been possible to prepare a syrup of polymerized methyl methacrylate in monomeric methyl methacrylate which has been stable, has had a useful viscosity, and has had a sufficiently high concentration of polymer such that it could be molded at a high rate to give laminated articles having good weathering, stiffness and craze-resistant properties.

According to the present invention, there is provided a polymer-in-monomer syrup wherein the said monomer is methyl methacrylate alone or with a copolymerizable α - β -ethylenically-unsaturated compound, wherein the polymer is a methyl methacrylate homopolymer or a copolymer of methyl methacrylate and a copolymerizable α - β -ethylenically-unsaturated compound, has an inherent viscosity as hereinafter defined within the range of 0.25 to 1 and is dissolved in the said monomer, and wherein the syrup has a bulk viscosity in the range 0.5 to 50 poises and contains less than

20 ppm of a polymerization initiator.

Whenever inherent viscosity is referred to in this specification, including the claims, the inherent viscosity should be determined at 20° C. in chloroform solution at a concentration of 0.50 grams/100 ml. according to the method described in F. W. Billmeyer, Textbook of Polymer Chemistry, Interscience Publishing, Inc. (1957) P. 128. The inherent viscosity of the polymer should be high enough to ensure good physical properties of the cured final products, but low enough for the syrup to have a relatively high polymer content, thus resulting in low shrinkage and low exothermicity, i.e. low heat of reaction, on curing, so as to facilitate fabrication into reinforced plastic structures. The inherent viscosity is preferably within the range 0.3 to 0.55.

Suitable α - β -ethylenically-unsaturated compounds which may be used to form copolymers with methyl methacrylate include vinyl acetate, styrene, alkyl acrylates, and other alkyl methacrylates. Methyl methacrylate, however, preferably constitutes at least 50% by weight of such copolymers.

The bulk viscosity of the syrup may be measured by any standard method, for instance the Gardner Tube or Brookfield Viscosimeter. The method used throughout this specification and claims has been to compare the samples with standard viscosity samples in Gardner viscosity tubes. The bulk viscosity of the syrup at 25° C. is preferably between 2 and 15 poises. The aforesaid low viscosity polymer may either be formed in sufficient monomer in situ or be prepared separately and dissolved in sufficient monomer to give the requisite bulk viscosity.

There is also provided, according to the present invention, a process comprising heating monomer in the presence of a chain transfer

agent, stopping the polymerization by cooling when the reaction mixture has a bulk viscosity of 0.5 to 50 poises at 25° C. and the polymer has an inherent viscosity of 0.25 to 1, and by using a polymerization initiator in a sufficiently small amount so that the final syrup contains less than 20 ppm of the initiator.

Any suitable free-radical polymerization initiator may be used, for example a peroxygen initiator, e.g., benzoyl peroxide, diethyl peroxide, diisobutyl peroxide, or an azo initiator, e.g., α - α' -azodiisobutyronitrile, α - α' -azobis (methylisobutyrate), and others described in U.S. specification 2,471,959. Even small amounts of surplus initiator (over 20 ppm) present in the syrup after the polymerization has been stopped by cooling will continue to initiate some polymerization, even at or below room temperature, although only at a slow rate, and therefore make the syrup unstable. We have found that it is very important that only just sufficient polymerization initiator be used so that practically none is left after the polymerization reaction. Less than 300 ppm of initiator is generally sufficient initially to obtain useful results in accordance with the invention.

Any suitable chain transfer agent may be used, for example, thiophenol, lauryl mercaptan or any other alkyl or aryl mercaptan. The chain transfer agent controls the polymerization and assists in obtaining a polymer of the desired inherent viscosity, since it is possible to quench the polymerization mixture quickly and stop the polymerization at the desired moment. The chain transfer agent may be present in amount 0.05 to 1 mole per cent., preferably 0.1 to 0.4 mole per cent.

The polymerization is preferably checked by using, as a quenching liquid, a cold solution of a polymerization inhibitor dissolved in the monomer. The appropriate amount of monomer to form the desired syrup may either be added wholly or partially as the quenching liquid, or at a later stage, so as to bring the syrup to the appropriate bulk viscosity.

Any suitable inhibitor may be used, for example hydroquinone, a catechol, pyrocatechol, and other known inhibitors that are soluble in the monomer. The cold quenching liquid preferably contains 0.001 to 1% by weight of the inhibitor. This amount of inhibitor in cold monomer, together with any cooling effected by a water jacket around the polymerization kettle, should be sufficient to reduce the temperature of the contents of the kettle to about 60° C. or lower, and thus check the polymerization. The amount of inhibitor in the final syrup is preferably 10 to 100 ppm.

An optional additional feature of the invention is that the syrup may be sold containing a suitable cross-linking agent, without affecting its stability. The fabricability, physical properties and weathering of the molded product are improved by the presence

of a cross-linking agent, particularly when fibrous reinforcement is used. The cross-linking agent may be added to the syrup in amounts of 0.1 to 20% by weight on the completion of the quenching. Any suitable poly-unsaturated cross-linking agent may be used, for example ethylene dimethacrylate, propylene dimethacrylate, polyethylene glycol dimethacrylate, divinyl benzene, triallyl cyanurate and diallyl phthalate.

Two factors govern the choice of conditions for a practical polymerization cycle. The conditions must be such that the polymerization rate is fast enough to be economically attractive, and secondly, the conditions must be such that the initiator is almost completely reacted. The polymerization rate can be calculated from the initiator concentration and temperature by equations well known in the chemical literature (see P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press (1953) P. 114). The approximate amount of initiator which can be added to the polymerization system and still not have too much remaining after syringing can be calculated in accordance with the formula $X = 10^{-3} 2^{Pt/H}$, where X is the weight per cent. of initiator added prior to polymerization, H is the half-life of the initiator, and Pt is the polymerization time.

According to one embodiment of the invention, a syrup of suitable viscosity may be produced by preparing the polymer *in situ* by heating the monomer, preferably wholly methyl methacrylate, in a stirred jacketed kettle under reflux, at atmospheric pressure in the presence of a predetermined small amount of initiator and chain transfer agent. This solution may be heated at between 50 and 150° C., preferably 95 to 105° C., until the predetermined viscosity of the solution has been obtained and until the initiator content has been reduced to below 20 ppm. The polymerization may then be stopped by the addition of from 1 to 10 parts by weight of cold methyl methacrylate containing sufficient hydroquinone to inhibit completely any further polymerization of the methyl methacrylate.

Since the resulting syrup is stable, it is suitable for sale to fabricators for use in their molding operations. The fabricator mixes the stable syrup with a suitable catalyst, and preferably a filler, and subjects the resulting mixture to a molding operation in which the syrup is cured to a solid shape as it is polymerized. The low exothermicity of the syrup makes it possible to process parts rapidly without blemishes such as bubbles and flow lines.

Prior art monomer-polymer syrups have been made by partially polymerizing methyl methacrylate without the use of transfer agents, without proper regard for the type and quantity of polymerization initiator, and without regard for the proper time and temperature of polymerization. Thus prior art syrups

5 have not been storable or shippable, and have
been relatively useless unless they have been
prepared on site for immediate use. An alter-
native method used previously has been to
10 prepare the methyl methacrylate polymer
separately, and then dissolve it as required in
methyl methacrylate monomer to produce
syrops of suitable viscosity. Such separately
15 prepared polymers are expensive and have been
of inherent viscosity (0.44 to 2.0) such that it
has been possible to use only a limited con-
centration of polymer, and the resulting syrups
have therefore had relatively high shrinkage
and high exothermicity, in contrast with the
syrups of the present invention.

The following Examples further illustrate
the invention; all parts are by weight unless
otherwise noted.

EXAMPLE I

20 A stirred, water-jacketed kettle provided
with a reflux condenser was charged with 116
parts of inhibitor-free monomeric methyl
methacrylate and about 0.73 part of lauryl
mercaptan. The resulting solution was heated
25 to 80°C. \pm 1°C. and then 0.0363 part of α ,
 α ' azobisisobutyronitrile dissolved in 5.0 parts
of methyl methacrylate added. The jacket tem-
perature was adjusted to 100°C. \pm 1°C. and

the kettle contents were allowed to reach reflux
temperature, ca. 103°C. Samples were taken
periodically from the reaction mixture and
measured for viscosity. When the viscosity
reached about 20 poises, (on a sample cooled
to 25°C.), the reaction was quenched by the
addition of a 25°C. solution containing
0.00328 part of hydroquinone dissolved in 10.0
parts of methyl methacrylate. This point was
reached in about 40 minutes after addition of
the initiator.

The resulting syrup contained no detectable
initiator, had a viscosity of about 20 poises at
25°C., had a polymer content of about 35%,
an inherent viscosity of about .32, a molecular
weight of about 50,000, and a good shelf
stability, i.e., substantially no color change or
viscosity change after 30 days.

The process of Example I was substantially
duplicated for the preparation of other syrups
of the same inhibitor content (25 ppm), all of
which had excellent stability and shelf lives.
The results are given in the Table as Examples
2—6, 8 and 9, and are compared with Example
7 which latter is not according to the invention,
a relatively large amount of polymerization
initiator having been used as a contrast.

TABLE

Example	Initiator		Chain-Trans. Agent		Cycle Min. at °C. (.5 g/100 cc)	Inherent Visc. in Chloroform	Conver. %	Visc. at 25° C.	Storage Stability
	Kind	Amount (ppm)	Kind	Amount (%)					
2	(3)	242	(a)	.1	20 at 100	0.88	16.3	3.9	good
3	(3)	200	(b)	.04	47 at 100	0.51	—	—	good
4	(2)	300	(a)	.6	22 at 100	0.32	29.4	2.8	fair
5	(2)	500	(a)	.6	27 at 100	0.32	33.4	8.4	fair
6	(2)	300	(a)	.6	50 at 100	0.32	38.3	13.5	good
7	(1)	1000	(a)	.1	13 at 100	0.60	28.2	30.2	poor
8	(2)	132	(a)	.1	27 at 100	0.91	18.4	5.0	good
9	(2)	300	(a)	.45	45 at 100	0.39	32.0	12.0	good

(1) Methyl ester of (2)

(2) Alpha alpha' azo(methylisobutyrate)

(3) Benzoyl peroxide

(a) Lauryl mercaptan

(b) Thio phenol

The sirups of the invention are marketed as such for a multiplicity of uses in which suitable polymerization initiators are added to polymerize completely the monomer contained in the sirup. The final polymerization being conducted by techniques similar to those presently used in polyester laminating and potting technology. The sirups may be mixed with inert additives such as glass fibers, powdered metals, pigments, natural and synthetic fibers, and other toughening, filling, coloring and/or strengthening materials; sheets may be made by pouring the sirup on a corrugated or flat

15 surface before or after a fabric, metal or glass layer is placed on the surface; and the sirup may be used as a laminating layer for wood, plastic, and other surfaces. Subsequent to the aforesaid operations in matched metal molds, or by contact process, the sirup is polymerized under some pressure, e.g., 0.1 to 2,000 psi and temperatures between room temperature and 150° C., to substantially 100% polymer or by any other suitable molding process. For optimum properties, the products should be cured under elevated temperatures up to 125° C. and pressures up to 1,000 psi, until the

monomer content of the sirup has been reduced to a low level (preferably less than 1%). Where low pressures are used it is sometimes necessary to eliminate dissolved gases by evacuation of the sirup prior to use.

The methacrylate sirups of the invention, due to their remarkable stability, are capable of being shipped from the point of manufacture to the fabricator without undesirable polymerization of monomer content. The fabricator is able to store the sirup without danger of polymerization until he wishes to use it. The sirup can then be combined with the fibers,

fillers, etc. as described, molded, laminated or otherwise treated, without excessive exothermicity, to polymerize the monomer content to superior products.

5 WHAT WE CLAIM IS:—

1. A polymer-in-monomer syrup wherein the said monomer is methyl methacrylate alone or with a copolymerizable α - β -ethylenically-unsaturated compound, wherein the polymer is a methyl methacrylate homopolymer or a copolymer of methyl methacrylate and a copolymerizable α - β -ethylenically-unsaturated compound, has an inherent viscosity as hereinbefore defined within the range of 0.25 to 1 and is dissolved in the said monomer, and wherein the syrup has a bulk viscosity in the range 0.5 to 50 poises and contains less than 20 ppm of a polymerization initiator.

2. A syrup according to claim 1, wherein the methyl methacrylate constitutes at least 50% by weight of the said polymer.

3. A syrup according to claim 1 or 2, wherein the polymer has an inherent viscosity in the range of 0.3 to 0.55.

25 4. A syrup according to any of claims 1 to 3, wherein the syrup has a bulk viscosity in the range 2 to 15 poises.

5. A syrup according to any of claims 1 to 4, containing also a polymerization inhibitor.

30 6. A syrup according to claim 5, wherein the polymerization inhibitor is hydroquinone, a catechol or a pyrocatechol.

7. A syrup according to claim 5 or 6, wherein the polymerization inhibitor is present in an amount from 10 to 100 ppm based on the syrup.

8. A syrup according to any of claims 1 to 7, containing also a cross-linking agent.

40 9. A syrup according to claim 8, wherein the cross-linking agent is present in an amount up to 20% by weight based on the syrup.

10. A syrup according to claim 8 or 9, wherein the cross-linking agent is ethylene dimethacrylate, propylene dimethacrylate, polyethylene glycol dimethacrylate, divinyl benzene, triallyl cyanurate or diallyl phthalate.

45 11. A polymer-in-monomer syrup according to any of claims 1 to 10 substantially as hereinbefore described.

50 12. A polymer-in-monomer syrup substantially as described in any of the foregoing

Examples 1 to 6, 8 or 9.

13. A polymerization product obtained by curing a syrup according to any of claims 1 to 12 in the presence of a cross-linking agent.

14. A process for preparing a syrup according to any of claims 1 to 12, comprising heating monomer in the presence of a chain transfer agent, stopping the polymerization by cooling when the reaction mixture has a bulk viscosity of 0.5 to 50 poises at 25° C. and the polymer has an inherent viscosity of 0.25 to 1, and by using a polymerization initiator in a sufficiently small amount so that the final syrup contains less than 20 ppm of the initiator.

15. A process according to claim 14, wherein the polymerization is stopped by quenching with a cold solution of a polymerization inhibitor dissolved in monomer.

16. A process according to claim 15, wherein the cold quenching solution contains 0.001 to 1% by weight of the inhibitor.

17. A process according to any of claims 14 to 16, wherein the initiator is benzoyl peroxide, α - α' -azodiisobutyronitrile or α - α' -azo-bis(methylisobutyrate).

18. A process according to any of claims 14 to 17, wherein the amount of initiator initially present is less than 300 ppm.

19. A process according to any of claims 14 to 18, wherein the chain transfer agent is lauryl mercaptan or thiophenol.

20. A process according to any of claims 14 to 19, wherein the chain transfer agent is present in amount from 0.05 to 1 mole per cent.

21. A process according to any of claims 14 to 20, wherein the said heating is carried out under reflux.

22. A process according to any of claims 14 to 21, wherein the said heating is carried out at 50 to 150° C.

23. A process according to any of claims 14 to 22, substantially as hereinbefore described.

24. A process substantially as described in any of Examples 1 to 6, 8 or 9.

25. A polymerization product formed by curing a syrup prepared according to the process claimed in any of claims 14 to 24.

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